Thermochemical Modeling of Advanced Nuclear Fuels

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Objective: To develop a comprehensive thermochemical models of advanced nuclear fuel systems. The models will be predictive with regard to phase formation and chemical activities during high temperature processing/fabrication, identifying product formation and potentially problematic vapor pressures. The models will also determine phase formation, melting behavior, and chemical activities of fuel, bred actinides, and fission products to allow prediction of material transport and chemical interactions.

Background: The high temperature processing and burnup of nuclear fuel has presented substantial chemical challenges, and chemical models for fuel under these conditions have been important for optimizing processing, designing for optimal in-reactor behavior, and for determining behavior and release under accident conditions. Nominal UO_2 fuel has been intensively studied and a consensus phase diagram in the U-O system exists. The development of thermochemical models for $UO_{2\pm x}$ has been the subject of significant effort over the past 30 years, culminating in several useful models using a variety of approaches. For advanced fuels, such as those containing uranium carbide(s), much more limited work has been done, although there are simple models of the carbides. Given recent issues in carbide containing fuels there may be a need for substantially more accurate and sophisticated models of these systems.

Processing issues for advanced, non-oxide containing fuels have been significant. A system of current interest for particulate fuels is two-phase, consisting of MO_2 and MC_2, which allows oxygen released during fission to be captured in forming an actinide oxide from the carbide, rather than increasing the pressure in the particle through formation of CO. Production of the two-phase fuel has been problematic in terms of identifying appropriate equilibrium compositions, obtaining adequate sintering, unwanted carbothermal reduction of the oxide, and carbon transport, among others. Currently, there is no comprehensive thermochemical model that would allow easy calculation of activities/pressures, stable equilibrium phases, and other important parameters.

LWR and CANDU technologies have benefited from the low burnup and modest operating temperatures that simplify their chemical behavior. The low fission product yield and temperature has resulted in non-noble fission products remaining dissolved in the urania and in limited mobility. Advanced fuels are expected to operate at substantially higher temperatures and to greater burnups. The result will be significant secondary phase formation other than noble metals. Specifically, fission product-fuel oxide phases will form, depending on initial fuel composition, burnup, fission product distribution, and the presence of secondary materials such as carbide fuel phase(s) and carbon or other materials present as clad/coatings. All these effects are complicated by the transport properties of the various species that are formed, and therefore can

deplete/concentrate in thermally or chemically differentiated regions. Without a thorough understanding of the chemical state of the fuel it will be impossible to predict species transport within the fuel.

Currently, there is no comprehensive model that will accurately predict phase formation and activities/vapor pressures during burnup and under accident conditions for advanced fuels. A model system for CANDU and LWR fuel has been undergoing development, and for which significant progress has been made. This includes models of the solution phases of the metals and oxides within the fuel. Given the systems investigated are LWR or CANDU fuels with low burnups and moderate temperatures, all oxide phases are in a single uranate-rich solution phase, which would not be the case at much higher burnups where relatively independent oxide fission product phases can form. In addition, oxide solution phases tend not be ideal solutions as there are significant energetic interactions, and this has traditionally made them difficult to model.

Approach: The processing of advanced fuels that contain non-oxide phases and/or significant concentrations of other actinides such as plutonium, will require accurate thermochemical models to allow efficient and reproducible production. Actinide oxide solid solutions have been repeatedly demonstrated to not be accurately modeled by simple ideal or even regular solution approaches. Early work at ORNL and in England, and more recent work at the Royal Military College in Canada, have substantially advanced understanding of the thermochemical behavior of these solid solutions. It is still necessary, however, to further develop techniques to move beyond just inclusion of plutonium and consider more closely thorium and other actinides. The ORNL approach of mixing variable stoichiometry fictive oxide species has been very successful, and this will be expanded to include other important constituents so that an inclusive fluorite structure actinide solid solution can be developed. This model will also allow extension into the liquid oxide, so that accurate models of liquid compositions can be established. This will enable, for example, computation of liquidus and solidus (melting) temperatures, which is key information for both processing and safety analysis. A comprehensive model of the oxide fluorite solution can be incorporated into a widely usable database for extensive application in processing, in-reactor behavior, and accident analyses.

The thermochemistry of carbide-containing advanced fuels was partially ascertained in early work, but the models are still far from complete. To aid in processing of mixed carbide-oxide fuels, which currently is still problematic, models of the fairly wide stoichiometric ranges for the carbide phases will need to be further developed. A conventional approach utilizing mixing vacancies with the stoichiometric phase has proved useful and will be expanded upon. Databases that will allow wide ranges of exploratory calculations for high temperature processing conditions will be developed.

As noted above, high burnups and operating temperatures will result in higher fission product concentrations and greater species mobility. The result will be formation of multiple oxide phases, depending on composition, containing multiple constituents. The very successful modified associate species approach to modeling complex oxide liquids

will be applied to these systems. The result will be models incorporated into databases that can be used to computed melting temperatures and chemical acitivities/vapor pressures. The solid solutions of these phases can be modeled with a variety of techniques such as the quasi-chemical model or compound energy formalism. A database that contains both the solid solution and liquid solution models would allow full representation of the actinide-fission product system that would be available both for understanding in-reactor behavior and for inclusion in accident analysis calculations. These can be combined with models for fission product noble metal inclusions that will comprehensively represent the fuel system in a reactor.